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(54) Title: SYNERGISTIC HERBICIDAL COMPOSITIONS OF METOLACHLOR

(57) Abstract

Herbicidal composition comprising the most active optical isomer of metolachlor, defined by Formula (A), and a synergistically effective amount of at least one other herbicide selected from the substance classes of sulfonylureas and sulfonanilides as defined by Formula (I), triazines, triazinones and pyridazinones as defined by Formula (II), organophosphates, aryloxyalkanoic acids, aryloxyphenoxypropanoic acids, pyridine carboxylic acids, benzoic acids, diphenylethers and imidazolinones as defined by formula (III), dinitroanilines and benzonitriles as defined by Formula (IV), chloroacetanilides, benzothiadiazinones, thio- or biscarbanates and ureas as defined by Formula (IV), cyclobaranatics and acids at the second control of the second c

mula (V), cyclohexanedione-oximes as defined by Formula (VI) and bipyridyliums as defined by Formula (VII).

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SYNERGISTIC HERBICIDAL COMPOSITIONS OF METOLACHLOR.

The present invention relates to a novel herbicidal composition which comprises a combination of herbicidally active ingredients which is suitable for selectively controlling weeds in crops of useful plants, for example in crops of cereals, maize, rice, oilseed rape, sugar beet and sugar cane, in plantation crops, and in crops of cotton and soybeans.

The invention furthermore relates to a method of controlling weeds in crops of useful plants and to the use of this novel composition therefor.

Herbicidal compositions which comprise metolachlor in combination with other known herbicides are compiled, for example, in Research Disclosure No. 37242, April 1995.

Surprisingly, it has now been found that a combination of a certain optical isomer of metolachlor with at least one active ingredient from the abovementioned Research Disclosure, in a ratio varying within specific limits, has a herbicidal action which is capable of effectively controlling the majority of weeds occurring in crops of useful plants preemergence as well as postemergence without causing considerable damage to the useful plant.

The optical isomer of metolachlor which is suitable according to the invention is a RS,1'S(-)-N-(1'-methyl-2'-methoxyethyl)-N-chloroacetyl-2-eth yl-6-methylaniline, of the formula A

which is described, for example, in US-A-5 002 606.

Accordingly, the present invention provides a novel herbicidal composition for selectively controlling weeds which comprises, as active ingredient, the compound of the formula A

and a synergistically effective amount of at least one active ingredient from amongst the substance classes of the formula I

- N(CH₃)₂

(I)

in which

A is a radical of the formula

(A1)
$$(A2)$$
 CO_2CH_3
 $(A2)$
 CO_2CH_3
 CO_2CH_3

E is a radical of the formula

$$-\text{CO--NH--N} \\ \text{OCHF}_2 \\ \text{(E2)} \\ \\ \text{OCHF}_2$$

F (E7),
$$CI$$
 CI CH_3O_2C (E9)

of the formula II

in which

U-V is a radical of the formula CR₁=N, N=CR₁ or NR₁CO, in which

 R_1 is -NHC₃H₇-i, -NHC(CH₃)₂CN, -NHC₄H₉-t, -NHC₂H₅, -SCH₃, CH₃, -Cl,

W-Y is a radical of the formula $CR_2=N$, $N=CR_2$, NR_2CO or $CR_2=CR_3$, where R_2 is hydrogen, -Cl, -NH₂, -NHC₃H₇-i or -NHC₂H₅ and R_3 is -NH₂, -NHCH₃ or -O-CO-SC₈H₁₇ and

R is -Cl, -SCH₃, -C₄H₉-t,
$$\longrightarrow$$
 or hydrogen,

of the formula III

$$Q \left(\begin{array}{c} R_4 \\ C \\ R_5 \end{array} \right) CO - R_6 \tag{III}$$

in which

n is 0 or 1,

R₄ is hydrogen,

R₅ is hydrogen, -CH₃ or -NH₂,

 R_6 is hydroxyl, $-OC_2H_5$, $-O-CH(CH_3)_2-CO_2C_2H_5$, $-NHSO_2CH_3$, $-OCH_3$, $-OC_4H_9$ -n or

-OCH2-C=CH and

Q is a radical of the formula

(Q1)

(Q9)

 $-NHCH_2-P(O)(OM)_2$

(Q10)

, (Q2)

in which M is an alkali metal, ammonium, alkylammonium, sulfonium or alkylsulfonium,

$$CH_3O$$
 N OCH_3 OCH_3

$$\begin{array}{c} H \\ \downarrow \\ CH_3 \\ C_3H_7-i \end{array}$$

$$\begin{array}{c} CH_3-O-CH_2 \\ \downarrow \\ C_3H_7-i \end{array}$$

$$\begin{array}{c} H \\ CH_3 \\ C_3H_7-i \end{array}$$

$$\begin{array}{c} CH_3 \\ C_3H_7-i \end{array}$$

$$\begin{array}{c} CH_3 \\ C_3H_7-i \end{array}$$

$$\begin{array}{c} CH_3 \\ C_3H_7-i \end{array}$$

$$H_3C$$
 H
 CH_3
 C_3H_7
 C_3H_7

of the formula IV

$$R_{9}$$
 $\xrightarrow{5}$ R_{7} 6 $X - R_{11}$ (IV)

in which

R₇ is 2-NO₂ or 2-Br,

 R_8 is 6-NH₂ or 6-Br, or

 R_8 and R_7 together form a radical of the formula -CH(CH₃)₂-CH(OC₂H₅)O- which bridges positions 2 and 3 of the phenyl radical and where the carbon atom of this radical is linked with position 2 and the oxygen atom of this radical with position 3,

R₉ is 3-CH₃, 4-CF₃ or 4-CN,

R₁₀ is hydrogen or 4-CH₃,

X is -O-, -NH-, -NC₃H₇-n- or -NC₂H₅- and

 R_{11} is hydrogen, -CH(C₂H₅)₂, -C₃H₇-n, -CH₂-C(CH₃)=CH₂, -CO-C₈H₁₇-n, -CO-C₇H₁₅-n or -SO₂CH₃,

of the formula V

$$R_{12}$$

Z-N-CO- R_{13} (V)

in which Z is a radical of the formula

CH₃ CI CI, CI, CI, CF₃ (Z2) (Z3)

$$\begin{array}{c} CH_3 \\ CH_3 \\ CF_3 \\ CG_2 \\ CG_3 \\ CG_3 \\ CG_4 \\ CG_5 \\ CG_6 \\$$

$$CH_3$$
 CH_3 , $-CH_2-C_3H_7-i$, $-C_3H_7-n$, $-C_4H_9-n$, $(Z8)$ $(Z9)$ $(Z10)$ $(Z11)$ $(Z12)$ $(Z13)$

-CH₂
$$\longrightarrow$$
 or -C₃H _{\mathcal{T}} i, (Z16)

 R_{12} is hydrogen, -CH₂OCH₃, -CH₂OC₂H₅, -CH(CH₃)CH₂OCH₃, -C₃H₇-i, -CH₂-C₃H₇-i, -CH₂-C₃H₇-i, -CH₃ or -C₂H₅,

 $R_{13} \text{ is -N(CH}_3)_2, \text{-N(OCH}_3)\text{CH}_3, \text{-CH}_2\text{Cl}, \text{-SC}_2\text{H}_5, \text{-SC}_3\text{H}_7\text{-n}, \text{-OCH}_3, \text{-OC}_2\text{H}_5 \text{ or }$

 R_{13} together with R_{12} forms a radical of the formula -O-CH₂-C(CH₃)₂-CO-,

-SO
$$_2$$
-NH CO--CH $_2$ -CH(CH $_2$ Cl)-CHCl-CO- or

of the formula VI

$$\begin{array}{c|c}
 & X_1 \\
 & \parallel \\
 & C \\
 & R_{15}
\end{array} \quad (VI)$$

in which

R₁₄ is hydrogen or -CH₂-CH(CH₃)-SC₂H₅,

$$R_{15}$$
 is $-C_2H_5$, $-C_3H_7$ -n or $-C_2CH_3$, and

 X_1 is =0, =NOC₂H₅ or =NOCH₂-CH=CHCl,

or of the formula VII

$$\mathsf{CH_3} \xrightarrow{\oplus} \mathsf{CH_3} \qquad 2\mathsf{X}_2^{\bigoplus} \qquad \qquad (VII)$$

in which X_2^{\ominus} is Cl^{\ominus} or $CH_3SO_3^{\ominus}$, as a mixture with each other.

It is entirely surprising that the combination of the compound of formula A with at least one compound of formulae I to VII is greater than the expected additive action against the weeds to be controlled and thus in particular enhances the activity range of both components in two respects:

On the one hand, the rates of application of the single compounds are reduced while the effectiveness is retained. On the other hand, the novel herbicidal combination also achieves a high degree of weed control where the single compounds have become no longer agriculturally effective at low rates of application. The consequence is a substantial broadening of the activity spectrum against weeds and an additional increase in the selectivity for the cultivated plants that is necessary and desirable in the event of unintentional overapplication of herbicide.

The novel herbicidal combination can be used against a great number of agriculturally important weeds in crops of cultivated plants, including Veronica, Galium, Papaver, Solanum, Chenopodium, Amaranthus, Xanthium, Abutilon, Ambrosia, Sagitaria, Ipomoea, Cassiastora, Datura stramonium, Sesbania exaltata and Sida spinosa. Furthermore, it has emerged that, after application of the compositions according to the invention, the compound of the formula A which they comprise is broken down more rapidly in the treated crop plants, in particular maize, than metolachlor, which is an important advantage.

The compositions according to the invention are suitable for all application methods conventionally used in agriculture, for example preemergence application, postemergence application and seed dressing.

The herbicide mixture according to the invention is preferably suitable for controlling weeds in crops of useful plants such as cereals, rape, sugar beet, sugar cane, in plantation crops, in rice, cotton and, in particular, maize and soybeans.

Crops are also to be understood as meaning those which have been made tolerant to herbicides or classes of herbicides by conventional breeding or genetic engineering methods.

The combination of active ingredients according to the invention comprises the active ingredient of the formula A and the active ingredient(s) from the substance classes of the formulae I to VII in any ratio, but, as a rule, with an excess of one component over the other. Preferred mixing ratios of the active ingredient of the formula A to the other components are, as a rule, between 120:1 and 1:3.

It has been found that very particularly effective synergistic mixtures of active ingredients are the following combinations:

compound of the formula A + atrazine, compound of the formula A + cyanazine, compound of the formula A + flumetsulam, compound of the formula A + gluphosinate, compound of the formula A + glyphosate, compound of the formula A + metosulam, compound of the formula A + nicosulfuron, compound of the formula A + pendimethalin, compound of the formula A + rimsulfuron, compound of the formula A + sulfosate, compound of the formula A + terbuthylazine or compound of the formula A + 2,4-D, compound of the formula A + bromoxynil, compound of the formula A + dicamba, compound of the formula A + halosulfuron, compound of the formula A + metribuzine, compound of the formula A + paraquat, compound of the formula A + primisulfurone, compound of the formula A + prosulfurone, compound of the formula A + pyridate, compound of the formula A + rimsulfurone, compound of the formula A + simazine, compound of the formula A + sulcotrione or compound of the formula A + acetochlor, compound of the formula A + alachlor, compound of the formula A + ametryne, compound of the formula A + bentazone, compound of the formula A + butylate, compound of the formula A + clopyralide, compound of the formula A + BAY FOE 5043, compound of the formula A+ dimethenamide, compound of the formula A + EPTC, compound of the formula A + linuron, compound of the formula A + propachlor, compound of the formula A + thifensulfurone, compound of the formula A + trifluralin or compound of the formula A + bensulfurone. compound of the formula A +

chlorimuron-ethyl, compound of the formula A + chlorsulfurone, compound of the formula A + metsulfuron-methyl, compound of the formula A + sulfometuron-methyl, compound of the formula A + triasulfurone, compound of the formula A + tribenuron-methyl or compound of the formula A + imazaquin, compound of the formula A + imazaquin, compound of the formula A + imazapyr.

Preferred amongst these combinations of active ingredients are compound of the formula A + atrazine, compound of the formula A + cyanazine, compound of the formula A + flumetsulam, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + nicosulfuron, compound of the formula A + pendimethalin, compound of the formula A + rimsulfuron, compound of the formula A + sulfosate and compound of the formula A + terbuthylazine.

Another group of preferred combinations of active ingredients embraces compound of the formula A + atrazine, compound of the formula A + terbutylazine, compound of the formula A + flumetsulam, compound of the formula A + pendimethalin, compound of the formula A + metosulam, compound of the formula A + pyridate, compound of the formula A + pyridate + terbutylazine, compound of the formula A + glyphosphate, compound of the formula A + glufosinate, compound of the formula A + oxosulfuron and compound of the formula A + imazethapyr.

A further group of preferred combinations of active ingredients embraces compound of the formula A + cyanazine, compound of the formula A + nicosulfuron, compound of the formula A + rimsulfuron, compound of the formula A + sulfosate, compound of the formula A + dicamba, compound of the formula A + halosulfuron, compound of the formula A + primisulfuron and compound of the formula A + imazaquin.

Also of importance are the combinations compound of the formula A + primisulfuron + dicamba, compound of the formula A + prosulfuron + dicamba, compound of the formula A + prosulfuron + primisulfuron and compound of the formula A + prosulfuron + primisulfuron + dicamba.

The abovementioned combinations of active ingredients are preferably used in crops of maize.

A further group of preferred combinations of active ingredients is the following:

compound of the formula A + 2,4-D, compound of the formula A + gluphosinate, compound of the formula A + glyphosate, compound of the formula A + imazaquin, compound of the formula A + imazethapyr, compound of the formula A + metribuzin, compound of the formula A + pendimethalin, compound of the formula A + sulfosate or compound of the formula A + acifluorfen, compound of the formula A + bentazon, compound of the formula A + chlorimuron-ethyl, compound of the formula A + clethodim, compound of the formula A + clodinafop, compound of the formula A + clomazone, compound of the formula A + fenoxaprop, compound of the formula A + fluazifop, compound of the formula A + fomesafen, compound of the formula A + linuron, compound of the formula A + paraquat, compound of the formula A + quizalofop, compound of the formula A + sethoxydim or compound of the formula A + 2,4-DB, compound of the formula A + acetochlor, compound of the formula A + alachlor, compound of the formula A + dimethenamide, compound of the formula A + diuron, compound of the formula A + EPTC, compound of the formula A + ethalfluralin, compound of the formula A + imazapyr, compound of the formula A + lactofen, compound of the formula A + norflurazon, compound of the formula A + chloridazon, compound of the formula A + thifensulfuron-methyl, compound of the formula A + trifluralin or compound of the formula A + bensulfuron, compound of the formula A + chlorsulfuron, compound of the formula A + halosulfuron, compound of the formula A + metsulfuron-methyl, compound of the formula A + primisulfuron. compound of the formula A + prosulfuron, compound of the formula A + rimsulfuron, compound of the formula A + sulfometuron-methyl, compound of the formula A + triasulfuron, compound of the formula A + BAY FOE 5043, compound of the formula A + cloransulam, compound of the formula A + flumetsulam, compound of the formula A + oxosulfuron and compound of the formula A + tribenuron-methyl.

Amongst these, the preferred combinations of active ingredients are compound of the formula A + 2,4-D, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + imazaquin, compound of the formula A + imazethapyr, compound of the formula A + metribuzin, compound of the formula A + pendimethalin and compound of the formula A + sulfosate.

A further group of preferred combinations of active ingredients embraces compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the

formula A + imazethapyr, compound of the formula A + pendimethalin, compound of the formula A + oxosulfuron and compound of the formula A + flumetsulam.

The abovementioned combinations of active ingredients are particularly suitable for use in crops of soybeans.

Another group of preferred combinations of active ingredients is compound of the formula A + chloridazon, compound of the formula A + clethodim, compound of the formula A + clodinafop, compound of the formula A + clopyralid, compound of the formula A + cycloate, compound of the formula A + desmedipham, compound of the formula A + endothal, compound of the formula A + EPTC, compound of the formula A + ethofumesate, compound of the formula A + fenoxaprop, compound of the formula A + fluazifop, compound of the formula A + glufosinate, compound of the formula A + glyphosate, compound of the formula A + haloxyfop, compound of the formula A + metamitron, compound of the formula A + pebulate, compound of the formula A + phenmedipham, compound of the formula A + sulfosate and compound of the formula A + trifluralin.

These combinations are preferably suitable for use in sugar beet.

Furthermore of importance are the combinations of active ingredients compound of the formula A + clethodim, compound of the formula A + clodinafop, compound of the formula A + diuron, compound of the formula A + fluazifop, compound of the formula A + fluazifop, compound of the formula A + fluorentoridone, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + haloxyfop, compound of the formula A + norflurazon, compound of the formula A + prometryne, compound of the formula A + pyrithiobac, compound of the formula A + chloridazone, compound of the formula A + quizalofop, compound of the formula A + sethoxydim, compound of the formula A + sulfosate and compound of the formula A + trifluralin, in particular with a view to their application in cotton.

In addition to the compound of the formula A and at least one compound from amongst the substance classes of the formulae I to VII, the synergistic compositions according to the invention can comprise a safener. in particular benoxacor. The abovementioned active ingredients are described and characterized in "The Pesticide Manual", Tenth Edition, 1994, Crop Protection Publications or in other customary agronomical publications. Oxosulfuron (CGA 277 476) was introduced to the public at the Brighton Crop Protection Conference - Weeds - 1995 (Plenary Session 2, November 21, 1995).

The rate of application can vary within a wide range and will depend on the nature of the soil, the type of application (pre- or post-emergence; seed dressing; application to the seed furrow; no-tillage application etc.), the crop plant, the weed to be controlled, the respective prevailing climatic conditions, and on other factors governed by the type and timing of application and the target crop. In general, the mixture of active ingredients according to the invention can be applied in a rate of application of 300 to 4,000 g of mixture of active ingredients/ha.

In the composition according to the invention, the weight ratio of the component of the formula A to at least one compound from amongst the substance classes of the formulae I to VII is from 1:10 to 1:0.001.

If the composition comprises a safener, the weight ratio of herbicide of the formula (A) to safener is preferably 5:1 to 30:1.

The compositions according to the invention can be used in unmodified form, i.e. as obtained by synthesis, but they are preferably processed in a conventional manner with the auxiliaries conventionally employed in the art of formulation, for example to give emulsifiable concentrates, if they are not sulfonylureas, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. The types of application, such as spraying, atomizing, dusting, wetting, scattering or pouring, and the type of composition are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or products comprising the active ingredients of the formulae A and I, II, III, IV, V, VI or VII and, if desired, a safener and/or one or more solid or liquid formulation auxiliaries, are prepared in a manner known per se, for example by intimately mixing and/or grinding the active ingredients with the formulation auxiliaries, for example solvents or solid carriers. Furthermore, surface-active

compounds (surfactants) can additionally be used when preparing the formulations.

Suitable solvents may typically be: aromatic hydrocarbons, preferably the fractions containing 8 to 12 carbon atoms such as mixtures of alkylbenzenes, typically xylene mixtures or alkylated naphthalenes; aliphatic and cycloaliphatic hydrocarbons such as paraffins, cyclohexane or tetrahydronaphthalene; alcohols such as ethanol, propanol or butanol; glycols and their ethers and esters such as propylene glycol or dipropylene glycol ether; ketones such as cyclohexanone, isophorone or diacetone alcohol; strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or water; vegetable oils and their esters such as rapeseed oil, castor oil or soybean oil; and in some cases also silicone oils.

The solid carriers typically used for dusts and dispersible powders are usually natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. To improve the physical properties it is also possible to add highly dispersed silicic acid or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, including pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are materials such as calcite or sand. In addition, innumerable pregranulated materials of inorganic or organic origin may be used, especially dolomite or pulverised plant residues.

Depending on the type of compound of formula I to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties. Surfactants will also be understood as comprising mixtures of surfactants.

Suitable anionic surfactants may be water-soluble soaps as well as water-soluble synthetic surface-active compounds.

Suitable soaps are the alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts of higher fatty acids $(C_{10}-C_{22})$, e.g. the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can be obtained, inter alia from coconut oil or tallow oil. Further suitable soaps are also the fatty acid methyl taurin salts.

More often, however, so-called synthetic surfactants are used, especially fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth metal salts, ammonium salts or substituted ammonium salts, and they contain a C₈-C₂₂alkyl radical which also includes the alkyl moiety of acyl radicals, e.g. the sodium or calcium salt of ligninsulfonic acid, of dodecylsulfate, or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated or sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing 8 to 22 carbon atoms. Illustrative examples of alkylarylsulfonates are the sodium, calcium or triethanolamine salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid, or of a condensate of naphthalenesulfonic acid and formaldehyde.

Corresponding phosphates, typically salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 mol of ethylene oxide, or phospholipids, are also suitable.

Nonionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, or saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols.

Further suitable nonionic surfactants are the water-soluble polyadducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which polyadducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Illustrative examples of nonionic surfactants are nonylphenol polyethoxylates, polyethoxylated castor oil, polyadducts of polypropylene and polyethylene oxide, tributylphenol polyethoxylate, polyethylene glycol and octylphenol polyethoxylate.

Fatty acid esters of polyoxyethylene sorbitan are also suitable nonionic surfactants, typically polyoxyethylene sorbitan trioleate.

Cationic surfactants are preferably quaternary ammonium salts carrying, as N-substituent, at least one C_8 - C_{22} alkyl radical and, as further substituents, optionally halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates, for example stearyl trimethylammonium chloride or benzyl bis(2-chloroethyl)ethylammonium bromide.

The surfactants customarily employed in the art of formulation are described, inter alia, in "Mc Cutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, New Jersey, 1988, H. Stache, "Tensid-Taschenbuch" (Handbook of Surfactants), Carl Hanser Verlag, Munich/Vienna 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81.

The herbicidal compositions will usually contain from 0.1 to 99 % by weight, preferably from 0.1 to 95 % by weight, of a combination of the compound of formula A with the compounds of formula I, II, III, IV, V, VI or VII, from 1 to 99.9 % by weight of a solid or liquid adjuvant, and from 0 to 25 % by weight, preferably from 0.1 to 25 % by weight, of a surfactant.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The formulations may also contain further ingredients such as stabilisers, vegetable oils or epoxidised vegetable oils, (epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, typically silicone oil, preservatives, viscosity regulators, binders, tackifiers, as well as fertilisers or other chemical agents.

In particular, preferred formulations are made up as follows (throughout, percentages are by weight):

Emulsifiable concentrates

herbicidal combination:

1 to 90 %, preferably 5 to 20 %

surfactant:

1 to 30 %, preferably 10 to 20 %

liquid carrier:

5 to 94 %, preferably 70 to 85 %

Dusts:

herbicidal combination:

solid carrier:

0.1 to 10 %, preferably 0.1 to 5 %

99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

herbicidal combination:

water:

surfactant:

5 to 75 %, preferably 10 to 50 %

94 to 24 %, preferably 88 to 30 %

1 to 40 %, preferably 2 to 30 %

Wettable powders:

herbicidal combination:

surfactant:

solid carrier:

0.5 to 90 %, preferably 1 to 80 %

0.5 to 20 %, preferably 1 to 15 %

5 to 95 %, preferably 15 to 90 %

Granulates:

herbicidal combination:

solid carrier:

0.1 to 30 %, preferably 0.1 to 15 %

99.5 to 70 %, preferably 97 to 85 %

The invention is illustrated by the following non-limitative Examples.

Formulation Examples

Combinations of the compounds of formulae A, I, II, III, IV, V, VI or VII (throughout, percentages are by weight)

F1. Emulsifiable concentrates	a)	b)	c)	d)
combination of a compound of formula A and a herbicide of	5 %	10 %	25 %	50 %
formulae I to VII calcium dodecylbenzenesulfonate	6 %	8 %	6 %	8 %
polyethoxylated castor oil (36 mol EO)	4 %	-	4 %	4 %
octylphenol polyethoxylate	-	4 €	-	2 %

(7-8 mol EO)								
cyclohexanone	-		-		10		20	
mixture of aromatic hydrocarbons	85	ક્ર	78	8	55	ક	16	*
C_9 - C_{12}								•
· -								
Emulsions of any desired concentration can be pro-	epare	d by	dilutii	ng s	uch co	nce	entrate	s with
water.								
F2. Solutions	a)		b)		c)		d)	
combination of a compound of	E	¥	10	g.	50	9-	90	9.
formula A and a herbicide of	,	•	10	ъ	30	٠	30	·
formula I to VII								
1-methoxy-3-(3-methoxypropoxy)-			20	9-	20	9.	_	
propane	_		20	70	20	•		
polyethylene glycol 400	20	9.	10	<u> </u>	_		_	
N-methyl-2-pyrrolidone	_	•	_	·	30	ą.	10	8
mixture of aromatic hydrocarbons	75	ę.	60	9 .		-	_	
C ₉ -C ₁₂		Ū						
3 3 1 2								
The solutions are suitable for use as microdrops.								
F3. Wettable powders	a)		b)		c)		d)	
combination of a compound of	5	&	25	8	50	ક	80	8
formula A and a herbicide of								
formula I to VII								
sodium ligninsulfonate	4	ક્ર	-		3	¥	-	
sodium laurylsulfate	2	8	3	8	-		4	8
sodium diisobutylnaphthalene								
sulfonate	_		6	*	5	*	6 %	
octylphenol polyethoxylate	_		1	8	2	윰	-	
(7-8 mol EO)								
highly dispersed silica	1	8	3	8	5	¥	10	*
kaolin	88	8	62	*	35	ક	-	

The compound mixture is throughly mixed with the adjuvants and this mixture is ground in a suitable mill to give wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granulates	a)		b)		c)	
combination of a compound of	0.1	ક	5	8	15	8
formula A and a herbicide of				:		
formula I to VII				:		
highly dispersed silica	0.9	8	2	8	2	8
inorganic carrier	99.0	ક્ર	93	B	83	8
(Ø 0.1-1 mm)	•					
e.g. CaCO ₃ or SiO ₂						

The compound mixture is dissolved in methylene chloride, the solution is sprayed on to the carrier, and the solvent is removed under vacuum.

F5. Coated granulates	a)		b)		c)	
combination of a compound of formula A and a herbicide of	0.1	ક	5	8	15	8
formula I to VII						
polyethylene glycol 200	1.0	ક	2	용	3	*
highly dispersed silica	0.9	ક	1	¥	2	ક
inorganic carrier	98.0	£	92	ક્ષ	80	ક
(∅ 0.1 - 1 mm)						
e.g. CaCO ₃ or SiO ₂						

The finely ground compound mixture is uniformly applied in a mixer to the kaolin moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

F6. Extruder granulates	a)	b)		c)		d)	
combination of a compound of	0.1	£ 3	ક	5	£	15	8
formula A and a herbicide of	•						
formula I to VII							
sodium ligninsulfonate	1.5	b 2	8	3	8	4	*
carboxymethyl cellulose	1.4	2	8	2	ક્ર	2	*
kaolin	97.0	93	8	90	용	79	8

The compound mixture is mixed with the adjuvants and the mixture is moistened with water. This mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	b)		c)	
combination of a compound of formula A and a herbicide of	0.1	1	8	5	8
formula I to VII					
talcum	39.9	49	8	35	8
kaolin	60.0	50	8	60	8

Ready for use dusts are obtained by mixing the compound mixture with the carriers on a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
combination of a compound of	3 %	10 %	25 %	50 %
formula A and a herbicide of				
formula I to VII				
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyethoxylate	-	1 %	2 %	_
(15 mol EO)				
sodium ligninsulfonate	3 %	3 %	4 %	5 %
carboxymethyl cellulose	1 %	1 %	1 %	1 %
37% aqueous formaldehyde	0.2 %	0.2 %	0.2	% 0.2 %
solution				
silicone oil emulsion	0.8 %	0.8 %	0.8	¥ 0.8 %

- 23 -

water

87 % 79 % 62 % 38 %

The finely ground compound mixture is homogeneously mixed with the adjuvants to give a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

It is often more expedient to formulate the compound of formula A and the components of formula I to VII individually and only to combine them shortly before application in the applicator in the desired mixture ratio as tank mixture.

It can further prove advantageous to apply the active ingredient of the formula A, if desired in combination with the safener; separated in time from one or more active ingredients of the formulae I to VII. It is also possible to apply the active ingredient of the formula A separated in time from one or more active ingredients of the formulae I to VII, if desired in combination with the safener. The results obtained for the compositions according to the invention show an increased selectivity with respect to the crop plants in comparison to corresponding mixtures as in the abovementioned Research Disclosure.

Biological Examples

Example B1: Postemergence test:

Monocotyledon and dicotyledon test plants are grown in the greenhouse in plastic pots containing standard soil and, at the 4- to 6-leaf stage, sprayed with an aqueous suspension of the test substances prepared from a 25 % wettable powder (Example F3.), which corresponds to a dose of 2,000 g of a.i./ha (500 l of water/ha). The test plants are then grown on in the greenhouse under optimal conditions. After a test period of approximately 18 days, the test is evaluated using a nine-step assessment scale (1 = complete damage, 9 = no action). Assessment grades from 1 to 4 (in particular 1 to 3) describe a good to very good herbicidal action. In this test, the compositions according to the invention have a potent herbicidal action. The same results are obtained when the compositions according to the invention are formulated as described in Examples F1 to F2 and F4 to F8.

Example B2: Herbicidal action before emergence of the plants

Monocotyledon and dicotyledon test plants are sown in plastic pots in standard soil. Immediately after sowing, the test substances are sprayed on in the form of an emulsion concentrate (Example F1.) in the dose shown in Table 1 (500 l of water/ha). The test

WO 96/32013 PCT/EP96/01431

- 24 -

plants are subsequently grown in the greenhouse under optimal conditions. After a test period of 4 weeks, the test is evaluated: 100 % means complete damage, 0 % means no action. 100 % to 80 % and, in particular, 100 to 85 %, describe a good to very good herbicidal action.

Table 1

Tables 1 to 4: Preemergence treatment

Compound of the formula A in g/ha
Other component in g/ha

A in g/ha	600	400	200	100	50
Flumetsulam in g/ha	30	30	30	30	30
Maize	10	o	0	0	0
Cyperus	80	60	60	20	
Panicum	95	95	60 70	30 30	20 0
Metolachlor in g/ha					
Other component in g/ha					
Metolachlor in g/ha	600	400	200	100	50
Flumetsulam in g/ha	30	30	30	30	30
Maize	10	0	0	0	0
Cyperus	70	50	20	20	20
Panicum	98	70	60	30	30

Table 2

Compound of the formula A in g/ha

Other component in g/ha

A in g/ha	600	400	200	100	50
Imazethapyr in g/ha	30	30	30	30	30
				:	
Maize	20	20	20	20	20
Brachiaria	100	100	95	95	95
Cyperus	100	100	70	60	60
Panicum	100	100	95	90	90
Metolachlor in g/ha					:
Other component in g/ha					
Metolachlor in g/ha	600	400	200	100	50
Imazethapyr in g/ha	30	30	30	30	30
Maize	25	25	20	20	20
Brachiaria	100	95	95	85	75
Cyperus	100	70	70	60	60
Panicum	98	95	80	80	80

Table 3

Compound of the formula A in g/ha

Other component in g/ha

	_	•			
A in g/ha	600	400	200	100	50
Oxosulfuron in g/ha	30	30	30	30	30
Maize	80	70	70	70	70
Brachiaria	98	98	95	90	90
Cyperus	100	80	60	50	20
Panicum	98	98	95	60	50
Metolachlor in g/ha					
Other component in g/ha					
Metolachlor in g/ha	600	400	200	100	50
Oxosulfuron in g/ha	30	30	30	30	30
Maize	80	70	75	75	70

Brachiaria	90	98	80	80	80
Cyperus	95	40	30	20	20
Panicum	98	90	90	60	60

Table 4

Compound of the formula A in g/ha

Other component in g/ha

A in g/ha Pendimethalin in g/ha	600 125	400 125	200	100 125	50 125
Maize	0	0	0	0	0
Cyperus Panicum	70 100	70 95	50 95	30 95	0 95
Metolachlor in g/ha Other component in g/ha					
Metolachlor in g/ha Pendimethalin in g/ha	600 125	400 125	200 125	100 125	50 125
Maize	0	0	0	0	0
Cyperus	60	50	40	20	0
Panicum	100	95	95	80	80

The compositions according to the invention have a pronounced herbicidal action. The same results are obtained when the compositions according to the invention are formulated as described in Examples F2 to F8.

Example B3: Combination of pre- and postemergence herbicidal action

Monocotyledon and dicotyledon test plants are sown in standard soil in plastic pots.

Immediately after sowing, each of them is sprayed with the compound of the formula A as an emulsion concentrate (Example F1.) in the dose shown in Table 2 (500 l of water/ha). The test plants are then grown in the greenhouse under optimal conditions. When the plants have reached the 2- to 3-leaf stage (fully developed leaves of the reference plant maize), they are sprayed with component 2 of the test combination, prepared from one of the abovementioned formulations F2 to F8, in the dose mentioned in the table (500 l of water/ha). The test plants are then grown on under optimal conditions. After a test period of approximately 5 weeks, the test is evaluated: 100 % describes complete damage, 0 % no action. 100 % to 80 % and, in particular, 100 to 85 %, describe a good to very good herbicidal action.

Table 5

Tables 5 to 9: Combination of pre- and postemergence application

Compound of the formula A in g/ha
Other component in g/ha

A in g/ha	600	400	200	100
Atrazine in g/ha	600	400	200	100
Maize	0	0	0	0
5 1: :		05	4.5	20
Brachiaria	80	95	45	
Sorghum bic.	95	95	45	20
Metolachlor in g/ha				
Other component in g/ha				
Metolachlor in g/ha	600	400	200	100
Atrazine in g/ha	600	400	200	100
Maize	10	0	0	0
Brachiaria	70	55	5	0
Sorghum bic.	75	45	5	0
-				

Table 6

Compound of the formula A in g/ha

Other component in g/ha

A in g/ha Metosulam in g/ha	600	400 60	200 30	100 15
Maize	5 	5	0	0
Brachiaria Sorghum bic.	97 85	60 80	30 30	30 30
Metolachlor in g/ha Other component in g/ha				
Metolachlor in g/ha Metosulam in g/ha	600 120	400 60	200 30	100 15
Maize	0	0	0	0
Brachiaria Sorghum bic.	90 85	35 40	5	0 0

- 32 -

Table 7

Compound of the formula A in g/ha

Other component in g/ha

A in g/ha	600 -	400	200	100
Terbuthylazine in g/ha	600	400	200	100
•				
Maize	0	0	0	. 0
Brachiaria	60	50	15	0
Sorghum bic.	60 .	50	15	0
Metolachlor in g/ha				
Other component in g/ha				
Metolachlor in g/ha	600	400	200	100
Terbuthylazine in g/ha	600	400	200	100
Maize	0	0	0	0
Brachiaria	55	20	5	0
Sorghum bic.	35	20	5	0

Table 8

Compound of the formula A in g/ha

Other component in g/ha A in g/ha Glyphosate in g/ha Maize Brachiaria Sorghum bic. Metolachlor in g/ha Other component in g/ha Metolachlor in g/ha Glyphosate in g/ha Maize Brachiaria Sorghum bic.

Table 9

Compound of the formula A in g/ha
Other component in g/ha

70	35	17	8.5
500	250	125	60
10	0	0	0
100	95	60	40
100	90	80	60
•			
70	35	17	8.5
500	250	125	60
10	0	0	0
98	60	40	10
95	90	60	50
	10 100 100 100 70 500	10 0 100 95 100 90 70 35 500 250 10 0	500 250 125 10 0 0 100 95 60 100 90 80 70 35 17 500 250 125 10 0 0 98 60 40

The compositions according to the invention have a pronounced herbicidal action. The same results are obtained when the compositions according to the invention are formulated as shown in Examples F2 to F8.

WHAT IS CLAIMED IS:

1. A herbicidal composition which comprises a compound of the formula A

and at least one active ingredient from the substance classes of the formulae I

in which

A is a radical of the formula

CO—N(CH₃)₂, (A2)
$$CO_{2}CH_{3}, (A2)$$

$$CI \qquad CO_{2}CH_{3}, (A2)$$

$$CI \qquad CO_{2}CH_{3}, (A3)$$

$$CH_{3} \qquad (A4)$$

$$CO_{2}CH_{3}, (A4)$$

$$CO_{2}CH_{3}, (A4)$$

$$CH_{2}$$

$$CO_{2}CH_{3}$$

$$(A7)$$

$$CH_{2}CH_{2}$$

$$CH_{2}CH_{2}$$

$$CH_{2}CH_{2}$$

$$CH_{2}CH_{2}$$

$$CH_{3}CH_{2}$$

$$(A10)$$

$$CH_{3}$$

$$CH_{$$

E is a radical of the formula

$$-CO-NH-N-OCH_3 -CO-NH-N-OCHF_2$$

$$(E1) -CO-NH-N-N-OCH_3 -CO-NH-N-N-OCH_3$$

$$-CO-NH-N-N-OCH_3 -CO-NH-N-N-OCH_3$$

$$-CO-NH-N-N-OCH_3 -CO-NH-N-N-OCH_3$$

$$(E3) -CO-NH-N-N-OCH_3 -CO-NH-N-N-OCH_3$$

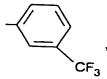
of the formula II

(II)

in which

U-V is a radical of the formula CR₁=N, N=CR₁ or NR₁CO, in which

 R_1 is -NHC₃H₇-i, -NHC(CH₃)₂CN, -NHC₄H₉-t, -NHC₂H₅, -SCH₃, CH₃, -Cl,



W-Y is a radical of the formula $CR_2=N$, $N=CR_2$, NR_2CO or $CR_2=CR_3$, in which R_2 is hydrogen, -Cl, -NH₂, -NHC₃H₇-i or -NHC₂H₅ and R_3 is -NH₂. -NHCH₃ or -O-CO-SC₈H₁₇ and

R is -Cl, -SCH₃, -C₄H₉-t,
$$\bigcirc$$
 or hydrogen,

of the formula III

$$Q \begin{pmatrix} R_4 \\ C \\ R_5 \end{pmatrix} CO - R_6$$
 (III)

in which n is 0 or 1,

R₄ is hydrogen,

R₅ is hydrogen, -CH₃ or -NH₂,

 $R_6 \text{ is hydroxyl, -OC}_2H_5, \text{-O-CH(CH}_3)_2\text{-CO}_2C_2H_5, \text{-NHSO}_2CH_3, \text{-OCH}_3, \text{-OC}_4H_9\text{-n or } C_4H_9\text{-n} \text{-} C_4H_9\text{-n}$

-OCH₂-C≖CH and

Q is a radical of the formula

-CH₂CH₂-P(O)(OM)CH₃

 $-NHCH_2-P(O)(OM)_2$

(Q1)

(Q2)

in which M is an alkali metal, ammonium, alkylammonium, sulfonium or alkylsulfonium,

$$-O \longrightarrow O \longrightarrow CF_3, -O \longrightarrow O \longrightarrow CI$$

$$-O \longrightarrow CI$$

$$CI \longrightarrow CI$$

$$CI \longrightarrow CI$$

$$CH_2CH_2-O \longrightarrow CI$$

$$CI \longrightarrow CI$$

$$CI \longrightarrow CI$$

$$(Q12)$$

$$CI \longrightarrow CI$$

$$(Q13)$$

$$CI \longrightarrow CI$$

$$(Q14)$$

of the formula IV

in which

R₇ is 2-NO₂ or 2-Br,

R₈ is 6-NH₂ or 6-Br, or

 R_8 and R_7 together form a radical of the formula -CH(CH₃)₂-CH(OC₂H₅)O- which bridges positions 2 and 3 of the phenyl radical and where the carbon atom of this radical is linked with position 2 and the oxygen atom of this radical with position 3.

R₉ is 3-CH₃. 4-CF₃ or 4-CN.

 $R_{10} \text{ is hydrogen or 4-CH}_3, \\ X \text{ is -O-, -NH-, -NC}_3H_7\text{-n- or -NC}_2H_5\text{- and} \\ R_{11} \text{ is hydrogen, -CH(C}_2H_5)_2, -C_3H_7\text{-n, -CH}_2\text{-C(CH}_3)\text{=CH}_2, -\text{CO-C}_8H_{17}\text{-n, -CO-C}_7H_{15}\text{-n} \\ \text{or -SO}_2\text{CH}_3, \\ \\$

of the formula V

$$R_{12}$$

Z-N-CO- R_{13} (V)

in which

Z is a radical of the formula

(Z11)

O-CONH—
O-CONH—
CH₃

(Z12)

(Z13)

$$-CH_2 \longrightarrow F$$
or
$$-C_3H_7-i$$
,
(Z16)

$$\begin{split} &R_{12} \text{ is hydrogen, -CH}_2\text{OCH}_3, \text{ -CH}_2\text{OC}_2\text{H}_5, \text{ -CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3, \text{ -C}_3\text{H}_{\mathcal{T}}\text{i, -CH}_2\text{-C}_3\text{H}_{\mathcal{T}}\text{i, -CH}_2\text{-C}_3\text{H}_{\mathcal{T}}\text{i, -CH}_3\text{ or -C}_2\text{H}_5, \\ &-\text{C}_3\text{H}_{\mathcal{T}}\text{n, -CH}_3\text{ or -C}_2\text{H}_5, \\ &R_{13} \text{ is -N}(\text{CH}_3)_2, \text{-N}(\text{OCH}_3)\text{CH}_3, \text{-CH}_2\text{Cl, -SC}_2\text{H}_5, \text{-SC}_3\text{H}_{\mathcal{T}}\text{n, -OCH}_3, \text{-OC}_2\text{H}_5 \text{ or } \end{split}$$

$$CH_2-O$$
 S
 C_3F

R₁₃ together with R₁₂ forms a radical of the formula -O-CH₂-C(CH₃)₂-CO-,

of the formula VI

in which

R₁₄ is hydrogen or -CH₂-CH(CH₃)-SC₂H₅,

$$R_{15}$$
 is -C₂H₅, -C₃H₇-n or $-$ SO₂CH₃ , and $-$ CI

 X_1 is =0, =NOC₂H₅ or =NOCH₂-CH=CHCl,

or of the formula VII

$$CH_3 \xrightarrow{\oplus} CH_3 \qquad 2X_2 \xrightarrow{\ominus} \qquad \qquad (VII)$$

in which X_2^{Θ} is Cl^{Θ} or $CH_3SO_3^{\Theta}$.

2. A composition according to claim 1, which comprises, as combination of active ingredients, compound of the formula A + atrazine, compound of the formula A + cyanazine, compound of the formula A + flumetsulam, compound of the formula A + gluphosinate, compound of the formula A + glyphosate, compound of the formula A + metosulam, compound of the formula A + nicosulfuron, compound of the formula A + pendimethalin, compound of the formula A + rimsulfuron, compound of the formula A + sulfosate, compound of the formula A + terbuthylazine or compound of the formula A + 2,4-D, compound of the formula A + bromoxynil, compound of the formula A + dicamba, compound of the formula A + halosulfuron, compound of the formula A + metribuzine, compound of the formula A + paraquat, compound of the formula A + primisulfurone, compound of the formula A + prosulfurone, compound of the formula A + pyridate, compound of the formula A + rimsulfurone, compound of the formula A + simazine, compound of the formula A + sulcotrione or compound of the formula A + acetochlor, compound of the formula A + alachlor, compound of the formula A + ametryne, compound of the formula A + bentazone, compound of the formula A + butylate, compound of the formula A + clopyralide, compound of the formula A + BAY FOE 5043, compound of the formula A+ dimethenamide, compound of the formula A + EPTC, compound of the ofrmula A + linuron, compound of the formula A + propachlor, compound of the formula A + thifensulfurone, compound of the formula A + trifluralin or compound of the formula A + bensulfurone, compound of the formula A + chlorimuron-ethyl, compound of the formula A + chlorsulfurone. compound of the formula A + metsulfuron-methyl. compound of the formula A + sulfometuron-methyl.

compound of the formula A + triasulfurone, compound of the formula A + tribenuron-methyl or compound of the formula A + imazaquin, compound of the formula A + imazapyr or compound of the formula A + imazapyr.

- 3. A composition according to claim 2, which comprises, as combination of active ingredients, compound of the formula A + atrazine, compound of the formula A + cyanazine, compound of the formula A + flumetsulam, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + metosulam, compound of the formula A + nicosulfuron, compound of the formula A + pendimethalin, compound of the formula A + rimsulfuron, compound of the formula A + sulfosate or compound of the formula A + terbuthylazine.
- 4. A composition according to claim 2, which comprises, as combination of active ingredients, compound of the formula A + atrazine, compound of the formula A + terbutylazine, compound of the formula A + flumetsulam, compound of the formula A + pendimethalin, compound of the formula A + metosulam, compound of the formula A + pyridate, compound of the formula A + pyridate + terbutylazine, compound of the formula A + glyphosphate, compound of the formula A + glufosinate, compound of the formula A + oxosulfuron or compound of the formula A + imazethapyr.
- 5. A composition according to claim 2, which comprises, as combination of active ingredients, compound of the formula A + cyanazine, compound of the formula A + nicosulfuron, compound of the formula A + rimsulfuron, compound of the formula A + sulfosate, compound of the formula A + dicamba, compound of the formula A + halosulfuron, compound of the formula A + primisulfuron, compound of the formula A + prosulfuron or compound of the formula A + imazaquin.
- 6. A composition according to claim 3, which comprises, as combination of active ingredients, compound of the formula A + primisulfuron + dicamba, compound of the formula A + prosulfuron + dicamba, compound of the formula A + prosulfuron + primisulfuron or compound of the formula A + prosulfuron + dicamba.
- 7. A composition according to claim 1, which comprises, as combination of active ingredients, compound of the formula A + 2,4-D, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + imazethapyr, compound of the formula A +

metribuzin, compound of the formula A + pendimethalin, compound of the formula A + sulfosate or compound of the formula A + acifluorfen, compound of the formula A + bentazon, compound of the formula A + chlorimuron-ethyl, compound of the formula A + clethodim, compound of the formula A + clodinafop, compound of the formula A + clomazone, compound of the formula A + fenoxaprop, compound of the formula A + fluazifop, compound of the formula A + fomesafen, compound of the formula A + linuron, compound of the formula A + paraquat, compound of the formula A + quizalofop, compound of the formula A + sethoxydim or compound of the formula A + 2,4-DB, compound of the formula A + acetochlor, compound of the formula A + alachlor, compound of the formula A + dimethenamide, compound of the formula A + diuron, compound of the formula A + EPTC, compound of the formula A + ethalfluralin, compound of the formula A + imazapyr, compound of the formula A + lactofen, compound of the formula A + norflurazon, compound of the formula A + chloridazon, compound of the formula A + thifensulfuron-methyl, compound of the formula A + trifluralin or compound of the formula A + bensulfuron, compound of the formula A + chlorsulfuron, compound of the formula A + halosulfuron, compound of the formula A + metsulfuron-methyl, compound of the formula A + primisulfuron, compound of the formula A + prosulfuron, compound of the formula A + rimsulfuron, compound of the formula A + sulfometuron-methyl, compound of the formula A + triasulfuron, compound of the formula A + BAY FOE 5043, compound of the formula A + cloransulam, compound of the formula A + flumetsulam, compound of the formula A + oxosulfuron or compound of the formula A + tribenuron-methyl.

- 8. A composition according to claim 7, which comprises, as combination of active ingredients, compound of the formula A + 2,4-D, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + imazethapyr, compound of the formula A + metribuzin, compound of the formula A + pendimethalin or compound of the formula A + sulfosate.
- 9. A composition according to claim 7, which comprises, as combination of active ingredients, compound of the formula A + gluphosinate, compound of the formula A + gluphosate, compound of the formula A + pendimethalin, compound of the formula A + oxosulfuron or compound of the formula A + flumetsulam.

- 10. A composition according to claim 1, which comprises, as combination of active ingredients, compound of the formula A + chloridazon, compound of the formula A + clethodim, compound of the formula A + clodinafop, compound of the formula A + clopyralid, compound of the formula A + cycloate, compound of the formula A + desmedipham, compound of the formula A + endothal, compound of the formula A + EPTC, compound of the formula A + ethofumesate, compound of the formula A + fluazifop, compound of the formula A + glufosinate, compound of the formula A + glyphosate, compound of the formula A + haloxyfop, compound of the formula A + metamitron, compound of the formula A + pebulate, compound of the formula A + phenmedipham, compound of the formula A + quizalofop, compound of the formula A + sethoxydim, compound of the formula A + sulfosate or compound of the formula A + trifluralin.
- 11. A composition according to claim 1, which comprises, as combination of active ingredients, compound of the formula A + clethodim, compound of the formula A + clodinafop, compound of the formula A + cyanazine, compound of the formula A + diuron, compound of the formula A + fluoreturon, compound of the formula A + gluphosinate, compound of the formula A + rorflurazon, compound of the formula A + prometryne, compound of the formula A + pyrithiobac, compound of the formula A + chloridazone, compound of the formula A + quizalofop, compound of the formula A + sethoxydim, compound of the formula A + sulfosate or compound of the formula A + trifluralin.
- 12. A composition according to claim 1, which comprises, as combination of active ingredients, benoxacor in addition to the compound of the formula A and at least one compound from the substance class of the formulae I to VII.
- 13. A composition according to claim 1, which comprises the compound of the formula A to at least one of the compounds from the substance class of the formulae I to VII in a weight ratio of 1:10 to 1:0.001.
- 14. A method of controlling undesirable plant growth in crops of useful plants, which comprises exposing the crop plant or its environment to a herbicidally active amount of a composition according to claim 1.

- 15. A method according to claim 14, wherein the exposure of the crop plant or its environment to the compound of the formula I, without or in combination with benoxacor, is separated in time from exposure to a compound of the formulae I to VII.
- 16. A method according to claim 14, wherein exposure of the crop plant or its environment to the compound of the formula I is separated in time from exposure to at least one compound of the formulae I to VII, without or in combination with benoxacor.
- 17. A method according to claim 14, wherein the crop plants are cereals, rice, oilseed rape, sugar beet, sugar cane, plantation crops, cotton and, in particular, maize and soybeans.
- 18. A method according to claim 14, wherein the crops of useful plants are treated with the abovementioned composition at rates of application which correspond to 0.3 to 4.0 kg of the total amount of active ingredient per hectare.

International Application No PCT/EP 96/01431

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 A01N37/22 A01N5 A01N43/50 A01N43/70 A01N57/20 A01N47/36 A01N47/12 A01N37/38 A01N37/34 A01N43/90 A01N43/40 //(A01N37/22,57:20,47:36,47:30,47:12,47:06,43:90, A01N33/18 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 6 A01N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Citation of document, with indication, where appropriate, of the relevant passages ... 1-18 RESEARCH DISCLOSURE, X no. 37242, - April 1995 pages 271-272, XP002012420 "Neue herbizide Mittel" CIBA-GEIGY AG: cited in the application see the whole document 1 - 18US,A,5 002 606 (MOSER HANS ET AL) 26 Υ March 1991 cited in the application see the whole document Patent family members are listed in annex. Further documents are listed in the continuation of box C. Х Special categories of cited documents: "I later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance เกษะกนิงก document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to earlier document but published on or after the international filing date involve an inventive step when the document is taken alone document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docudocument referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 1 8. 09. 96 3 September 1996 Authorized officer Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Ripswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni. Klaver, J Fax: (+31-70) 340-3016

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International Application No

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A. CLASSI IPC 6	FICATION OF SUBJECT MATTER 43:88,43:707,43:70,43:50,43:40,43:10,37	7:38,37:22,35:06,3	3:18)	
	o International Patent Classification (IPC) or to both national classification a	nd IPC		
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C. DOCUM	IENTS CONSIDERED TO BE RELEVANT			
Category *	Citation of document, with indication, where appropriate, of the relevant po-	assages	Relevant to claim No.	
Υ	DATABASE WPI		1-5, 11-18	
	Section Ch, Week 9520 Derwent Publications Ltd., London, GB	11-10		
	Class CO2, AN 95-151785	·		
	XP002012422 & JP,A,07 076 504 (IDEMITSU KOSAN CO	·		
;	, 20 March 1995	·		
	see abstract		•	
Υ	EP,A,O 318 433 (CIBA GEIGY AG) 31 May	1-18		
	See compounds of Formula I and IIIa.			
	see example B1; table A	·		
Υ	EP,A,O 282 613 (NISSAN CHEMICAL IND L	1-18		
	21 September 1988 see examples 4,6,9; tables 1,2			
	-/			
EVI Eur	ther documents are listed in the continuation of box C.	Patent family members are listed	in Annex.	
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which	is cited to establish the publication date of another 'Y' doc	cument of particular relevance; the nnot be considered to involve an in	claimed invention	
O' docum	nent reference to an oral disclosure, use, exhibition or do	cument is combined with one or ments, such combination being obvious	ore other such docu-	
'P' docurr	ent published prior to the international filing date but	the art. cument member of the same patent		
		Date of mailing of the international search report		
Name and	mailing address of the ISA Au	thorized officer		
European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rigwijk				
	Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl. Fax (+ 31-70) 340-3016			

International Application No PCT/EP 96/01431

ategory *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	DE,A,35 36 035 (HOECHST AG) 9 April 1987 see page 4, line 25 - line 63	1,7, 10-18
·		
	•	

Information on patent family members

International Application No PCT/EP 96/01431

Patent document cited in search report	Publication date			Publication date
US-A-5002606	26-03-91	CA-A- EP-A- JP-C- JP-B- JP-A-	1187901 0077755 1650377 3009899 58079964	28-05-85 27-04-83 30-03-92 12-02-91 13-05-83
EP-A-0318433	31-05-89 — .	AT-T- CA-A- DE-D- EP-A- ES-T- HR-A- JP-A- US-A-	115362 1329994 3852478 0608009 2065925 940507 1168603 5407898	15-12-94 07-06-94 26-01-95 27-07-94 01-03-95 30-06-96 04-07-89 18-04-95
EP-A-0282613	21-09-88	CA-A- EP-A- SU-A-	1289768 0361537 1572397	01-10-91 04-04-90 15-06-90
DE-A-3536035	09-04-87	NONE		

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